SCIENCE FOR GLASS PRODUCTION

UDC 666.1

A NEW TECHNOLOGY FOR PRODUCING FINELY DISPERSED GLASS BATCH AND THE CORRESPONDING GLASS MELTING PROCEDURE

V. F. Solinov[1] and Yu. M. Shershnev[1]

Translated from Steklo i Keramika, No. 2, pp. 3 – 6, February, 2005.

A batch preparation technology is proposed using traditionally prepared and mixed components with subsequent superfine milling of the mixture adding special temporary reactants. The milling method involves mechanical acceleration of the material and its self-milling. The crusher has high reliability parameters. A batch prepared in this way is homogeneous and ensures a fast completion of silicate formation reactions in the initial zone of the melting tank.

One of the critical technological stages in glass production is preparing raw materials in order to obtain a homogeneous batch, where mixing batch components is an essential factor of the batch quality.

Apart from the traditional method, there is known another method of batch preparation involving the premixing of the batch components, their subsequent treatment by aqueous solution of sodium hydroxide, and additional thermal treatment. The drawbacks of this method are the heterogeneous granulometric composition of components and the stratification of the batch.

Other methods for glass batch production, which prevent the heterogeneity and stratification of the batch by hydrothermal treatment and then drying and granulation of a "boiling layer" in the furnace, generate clots in the batch since its components react with moisture in different ways. Moreover, the said process involving an autoclave is complicated, and clots up to 5 mm and more are formed after sintering of the components.

We have developed a crusher with the required parameters operating without milling bodies. This crusher is capable of grinding a batch with a fraction up to 5 μm in a single stage. Such fine milling in traditional mills can be achieved only in several stages. The proposed crusher can mill materials of hardness up to 8 on the Mohs scale. The mining, fuel, chemical, construction, and other sectors of industry currently install bulky machines, usually multi-stage ones. Apart from consuming plenty of energy, another important problem of these plants is the fast consumption of milling bodies (balls, beaters, rolls, mill-stones) and armored lining.

Jet mills do not consume milling bodies. The idea of jet grinding is good but the cost of pneumatic transport is too high. Our idea was to replace pneumatic transport by a centrifugal force: to do this, we took two disks with cavities inside and connected them with material-feeding pipes. Next, we placed these disks opposite each other and made them rotate with a high speed in the opposite direction; material comes in between the disks and is accelerated by the centrifugal forces and pressed to the periphery of the disks, then a finely dispersed jet comes through a slot. The installed capacity of the proposed crusher is 27 kW with an output of at least 1 ton/h (or more for less hard materials).

The specifics and advantages of this crusher are the following:

Nontraditional crushing method. The crushing method consists in mechanical acceleration of the material and its self-grinding without participation of milling devices, which provides for low energy consumption on crushing, low wear of the working parts of the crusher, and prevents contamination of the finished product with metal. The crusher has a small size.

Simplicity and convenience of operation. Milling is performed intensely and continuously without compressed air or fast-wearing milling bodies (rollers, hammers, balls, and armored lining) that are usually made of special expensive high-alloy steel. The crusher has a moderate weight and size, a simple design, is convenient in servicing, and generates little noise. The design of the crusher provides for regulating the output and the fineness of milling.

[1] Scientific Research Institute of Technical Glass, Moscow, Russia; Scientific Technologies Co., Orel, Russia.

Reliability. The crusher has high reliability parameters: dependability, durability, and maintainability. No special tools are required for repair and maintenance. The preparation of the disks and the inner surfaces for an inspection takes a few minutes. The main units and parts are intended for long service life.

Cost effect. The crusher provides for a lower (compared to other crushing devices such as ball, roller, hammer mills, etc.) unit consumption of energy in milling, even in the case of very fine milling. The crusher takes a limited space and has a lower production and maintenance cost than other types of crushers.

This technology makes it possible to mechanically obtain a batch that is homogeneous at the molecular level. To achieve this, a traditional batch is subjected to dispersion until all its components are crushed to a particle size at least 5 μm, and in doing so the batch is saturated with additives: up to 30%. Under mechanical grinding of the batch components, free radicals (noncompensated bonds) are formed. In joint grinding of all batch components this role is played by the additives that act as temporary chemical elements linking other batch components, which generates a material without the free radical, whose homogeneity corresponds to the degree of dispersion of the mixture particles. Such a batch is inactive for the ambient medium. Thus, the additives act (before sintering of batch components) as a valence charge compensator; therefore, the batch has a homogeneous-equilibrium composition at the molecular level.

It should be noted that using this finely dispersed homogenous finely batch, silicate formation and complete homogenization of the mixture in a glass-melting furnace takes not more than 1 h.

Operation principle. A mixture of batch components with particle size ranging from 0.5 to 1.6 mm via the bin feeder gets into the crusher consisting of two disks rotating opposite each other. The mixture is ground at a high rate in a vortex flow in the presence of water. The joint grinding of all batch components together with water produces a homogeneous batch.

The advantages of the proposed technology are the following: the process of glass melt homogenization is eliminated from the glass melting procedure and the glass melting temperature decreases significantly (by 100 – 150°C), which makes it possible to extend the furnace campaign, since the silicate formation process starts in the dry form in the course of dispersing the batch and also due to the fine fraction of quartz sand.

At the present state of the glass-melting industry the reserves of raising glass strength by modifying its surface for developing compressive stresses are virtually exhausted, and the most critical is the problem of getting a homogeneous defect-free glass melt.

Unfortunately the effect of glass structure and its macro- and microstructural heterogeneities on its strength is insufficiently studied, since any technological processing in glass production, including the composition and method of batch preparation, the amount of recycled cullet, the furnace design and refractories, the melting temperature, etc. (the list continues) may influence the quality of glass melt.

The initial stage of melting silicate glass is constituted by chemical reactions between the batch materials known as silica formation. In the first stage of batch heating, at a temperature of around 300°C, before entering chemical reactions the batch components undergo several physical modifications: evaporation of moisture from the batch, dehydration of hydrates, thermal decomposition of some salts, transitions to other crystalline modifications. Later, with increasing temperature, quartz sand and alumina-bearing materials enter in chemical reactions and together with salts form various silicates, thus generating the primary glass melt. In the presence of this melt the chemical reactions between the batch components are significantly accelerated. At a temperature around 800°C the solid batch residues that have not passed into the melt but are impregnated with melted silicates and eutectics form a dense mass known as sinter. While most industrial glass compositions are heated up to 1200°C, the batch sinter melts and all silicate-formation processes are fully completed.

The dissolution of residual quartz in the primary melt resulting in the formation of silicate with a higher modulus, a gradually increasing silica content, and simultaneous mutual dissolution of silicates in each other constitute the glass formation stage. This melting phase is significantly slower than that of silicate formation. The time needed to complete glass formation for industrial glasses is at least 50% of the total duration of glass melting. This is due to the low rate of dissolution of residual quartz grains in a highly viscous silicate melt, since a highly viscous silica-saturated film is formed on the surface of the dissolving grains and impedes the diffusion processes. Accordingly, the most effective factors in accelerating glass formation are processes disturbing the film enveloping the quartz grains. Such processes include moving glass melt flows, as well as mixing, swirling, or spinning of the melt. Each temperature increase by 10°C up to 1550°C accelerates glass melting on the average by 5% and in the temperature interval of 1550 – 1600°C — by around 10%.

The removal of visible gaseous inclusions from the melt, i.e., the clarification of the melt is (conventionally) the next stage of glass melting following the glass-formation stage. The clarification of the melt can be intensified by maintaining the melt temperature at the maximum possible level. This not only decreases the degree of supersaturation of the melt by dissolved gases, but also significantly lowers the melt viscosity, which facilitates the rise of the bubbles to the melt surface and their exit from the melt.

The homogenization of the melt proceeds the most effectively in glass motion. In this case the boundary films of heterogeneous cells stretch into the finest layers with a highly extended specific area of contact. This facilitates mutual diffusion at the site of contact between the microcells and decreases the difference in their chemical compositions. This

glass-homogenizing effect is produced by moving glass melt flows, including organized (working flows, stirring, air-lift system) and spontaneous (natural convection, rise of gas bubbles toward the surface) ones.

The final phase in preparing the clarified and homogenized glass melt for working is its chilling, i.e., the cooling stage. After gradual cooling the glass melt reaches a temperature ensuring a viscosity required for producing glass articles. This process requires a high thermal homogeneity of the glass melt flow arriving to the working zone.

For industrial glass-melting furnaces classifying the glass-melting process into separate stages is arbitrary, since to a certain extent the specified stages proceed simultaneously; however, for each batch microvolume charged into the furnace the process of its gradual transformation into glass melt passes all five stages of glass melting.

The domestic and world practice of industrial glass melting traditionally applies the same method for producing silicate glass based on melting the batch and cullet charged into a furnace where the stages of silicate formation, glass formation, clarification, and homogenization occur on the surface of the glass melt in a heated melting tank. The traditional method for melting industrial glass involves a high energy consumption on melting (due to nonproductive heat consumption on maintaining the required temperature in the large volume of the melt permanently present in the furnace tank) and large capital investments to construct high-output furnaces.

Furthermore, the disadvantages of this technology include a substantial duration of the processes of glass formation, homogenization, and clarification of the melt and the presence of powerful uncontrolled convection flows leading to the transfer of a substantial amount of heat from the melting zone of the tank to the cooling zone, and the need to maintain high melting temperatures, in some cases exceeding the possibilities of contemporary refractories.

In view of the specified drawbacks, the main requirements on improving the glass-melting technology can be formulated as follows:

– decreasing specific power consumption; this can be achieved by removing the reactions between the batch components from the furnace and the highly viscous melt medium, as well as by decreasing the inert part of the melt that consumes up to 80 – 90% of the total heat supplied;

– developing optimum conditions for all glass-melting stages in each microvolume of the active part of the melt and the possibility of controlling these conditions.

The glass-melting method based on melting batch on an inclined tray, glass formation inside a thin overheated layer, and homogenizing the melt by forced stirring, which is proposed in USSR Inventor's Certificate No. 48551, is the closest to meeting the specified requirements. However, the idea of accelerating homogenization by stirring in a thin layer is hard to implement, whereas overheating of the melt inevitably facilitates the formation of secondary gas bubbles, which delay the clarification process.

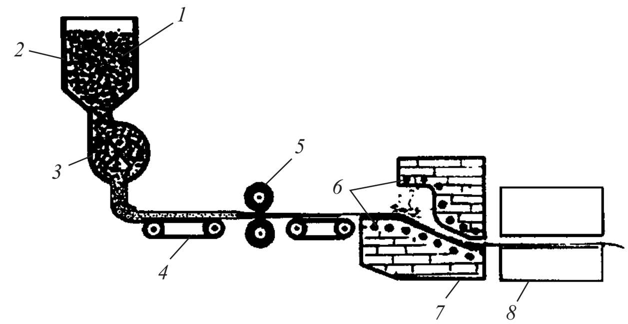

Fig. 1. Scheme of obtaining a uniform glass melt: *1*) traditional batch + cullet; *2*) receiving bunker; *3*) disperser; *4*) conveyor belt; *5*) shaping rollers; *6*) heaters; *7*) glass-melting plant; *8*) float tank.

A group of authors from the Scientific Research Institute of Technical Glass (Moscow), Saratov Institute of Glass (Saratov), Stromizmeritel' JSC (Nizhny Novgorod), and Scientific Technologies Co. (Orel) has put forward a method (Fig. 1) for obtaining a homogeneous defect-free glass melt in a direct monohomogeneous thin flow. As can be seen, traditional initial batch is fed from a bunker to a mechanical disperser, then is compressed as a plate, fed to the glass-melting plant, and finally to the float tank.

The phenomenon of mechanical activation of solid materials is known. Finely dispersed powder intensely milled by impact effects participates more actively in solid-phase reactions with other milled compounds due to its highly extended contact surface containing nonsaturated chemical bonds and active radicals.

We proposed a technology for producing batch from traditionally prepared and mixed components, including glass cullet, whose specific feature is subsequent superfine milling of the mixture with the introduction of special temporary reactants. Such batch preparation ensures its homogenization and makes the initial phases of the silicate-formation reactions occur in the course of mixing and be completed in the initial zone of the melting plant.

Information on this technology has been earlier described in more detail [1].

Experimental meltings were performed with batches of the following degree of milling: 1) traditional batch, 2 and 3) batch milled to the fraction of 100 – 150 and 5 μm, respectively.

Table 1 indicates the state of the batch depending on melting temperature.

The milling of batch components significantly affected the melting duration. Visual observation of the behavior of different compositions using disperse batch in melting established the increased intensity of compositions 1 and 2, all other terms being equal. The melting intensity of these compositions was manifested in their intense foaming, which produces a significant increase in the batch volume.

The advantage of the method proposed is the development of a fundamentally new method of glass melting. Its

TABLE 1

Batch	State of the batch at the temperature, °C				
	800	1000	1200	1300	1400
1	Beginning of silicate formation	Beginning of glass formation	End of glass formation	Clarification	Glass
2	End of silicate formation (sintering)	Middle of glass formation	Clarification	End of clarification	The same
3	Beginning of glass formation	End of glass formation	End of clarification	Glass	

use will make it possible to radically decrease the energy consumption on the glass-melting process, increase the specific output of glass melt, and decrease the capital investment in constructing plants for glass-melting due to the forced stabilization of the technological conditions of glass melting.

Another serious issue is lowering the content of equipment-induced iron in the batch. In dispersion all surfaces contacting with the batch are lined by ceramics based on Al_2O_3.

Another direction that completely eliminates the problem of batch contamination with metals consists in introducing additives generating the emission of gaseous hydrogen chloride into the batch. Hydrogen chloride interacts with iron and other metal oxides adsorbed and absorbed by quartz and, as a consequence, volatile iron and other metal chlorides are formed which intensely evaporate from the reaction mixture. Furthermore, bivalent iron gets oxidized to trivalent. The insignificant volume of the surface layer of sodium silicate compared to the content of titanium in the surface impurities volume prevents the formation of insoluble calcium silicates, which, in turn, ensures the clarity of quartz grains.

The method for preparing finely dispersed glass batch and the method for melting glass from this batch are protected by Eurasian patents Nos. 004463 and 004516 (2004).

REFERENCES

1. V. F. Solinov, "New concepts of glass-melting processes," *Steklo Keram.*, No. 10, 5 – 7 (2004).